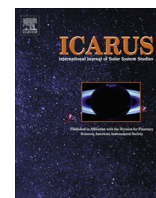


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Pathways for energization of Ca in Mercury's exosphere

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ABSTRACT

We investigate the possible pathways to produce the extreme energy observed in the calcium exosphere of Mercury. Any mechanism must explain the facts that Ca in Mercury's exosphere is extremely hot, that it is seen almost exclusively on the dawnside of the planet, and that its content varies seasonally, not sporadically. Simple diatomic molecules or their clusters are considered, focusing on calcium oxides while acknowledging that Ca sulfides may also be the precursor molecules. We first discuss impact vaporization to justify the assumption that CaO and Ca-oxide clusters are expected from impacts on Mercury. Then we discuss processes by which the atomic Ca is energized to a 70,000 K gas. The processes considered are (1) electron-impact dissociation of CaO molecules, (2) spontaneous dissociation of Ca-bearing molecules following impact vaporization, (3) shock-induced dissociative ionization, (4) photodissociation and (5) sputtering. We conclude that electron-impact dissociation cannot produce the required abundance of Ca, and sputtering cannot reproduce the observed spatial and temporal variation that is measured. Spontaneous dissociation is unlikely to result in the high energy that is seen. Of the two remaining processes, shock-induced dissociative ionization produces the required energy and comes close to producing the required abundance, but rates are highly dependent on the incoming velocity distribution of the impactors. Photodissociation probably can produce the required abundance of Ca, but simulations show that photodissociation cannot reproduce the observed spatial distribution.

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1. Introduction

Calcium was first detected in Mercury's exosphere by [Bida et al. \(2000\)](#) and was shown to be extremely energetic ([Bida et al., 2000](#); [Killen et al., 2005](#)). [Killen et al. \(2005\)](#) derived a temperature of Mercury's calcium exosphere of >20,000 K based on the measured line profiles from ground-based observations. Observations by the MESSENGER spacecraft confirmed the energetic nature of the exospheric Ca and showed that it predominately originates in the equatorial dawn hemisphere ([Vervack et al., 2010](#); [Burger et al., 2012](#)). [Burger et al. \(2014\)](#) modeled data obtained by the MESSENGER Ultraviolet and Visible Spectrometer (UVVS) during the primary and first extended missions, including data from March 18, 2011, through March 17, 2013. These data from portions of nine Mercury years showed that calcium is persistently ejected from the dawn equatorial region at speeds greater than Mercury escape velocity (4.25 km/s). The derived velocity distribution corresponds to a temperature ~70,000 K based on the velocities required to populate the highest altitudes before the calcium is ionized. These energies are surprising because the previously proposed source

processes (impact vaporization, photon-stimulated desorption, electron-stimulated desorption, and sputtering) produce much cooler ejecta ([Killen and Ip, 1999](#); [Killen et al., 2007](#)). In a previous paper [Killen et al. \(2005\)](#) proposed that the hot Ca is the result of dissociation of Ca-bearing molecules. [Killen and Hahn \(2015\)](#) showed that the source rate for atomic Ca and its variation with Mercury's true anomaly angle derived by [Burger et al. \(2014\)](#) from MESSENGER observations is consistent with impact vaporization by the influx of interplanetary dust and, in addition, a cometary stream associated with Comet 2P/Encke. A follow-on paper that traced cometary dust under the influence of gravity and Poynting–Robertson drag ([Christou et al., 2015](#)) showed that the enhanced emission near true anomaly angle 25° is consistent with impacts due to a comet stream associated with Comet 2P/Encke. However, there has never been a study of the energization mechanisms that could be responsible for producing such extremely hot calcium vapor.

Although several processes have been discussed in the literature for ejection of surface-derived atoms into exospheres, none of these processes, including electron-stimulated desorption, photon-stimulated desorption, impact vaporization or sputtering, can produce an exosphere in excess of 70,000 K, and confined to the dawn equatorial hemisphere, as measured for the Ca exosphere

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at Mercury (e.g. [Burger et al., 2014](#)). We therefore propose a two-step process in which the initial process ejects calcium-bearing molecules and the second process produces highly energetic atomic Ca. The purpose of this paper is to discuss possible pathways for energization of atomic calcium.

To have escape velocity, the Ca fragment must have an energy of >3.77 eV. If the hot Ca in Mercury's exosphere is 70,000 K, then the average energy of the Ca atom must be 5.6 eV. We investigate the pathways by which neutral molecules containing Ca can be dissociated into energetic fragments and we investigate the excess energies for each proposed process. In addition to the fact that Ca in Mercury's exosphere is very hot, any mechanism must explain the additional observations that Ca is seen almost exclusively on the dawnside of the planet centered on the equator, and that its content varies seasonally, not sporadically.

We first discuss impact vaporization and justify our assumption that CaO and Ca-oxide clusters are the major calcium-bearing ejecta. We then discuss pathways for dissociation and energization of the fragments: (1) electron-impact dissociation of CaO molecules, (2) spontaneous dissociation of Ca-bearing molecules following impact vaporization, (3) dissociative ionization, and (4) photo-dissociation. We briefly discuss sputtering.

2. Impact vaporization producing Ca-oxide clusters

[Killen and Hahn \(2015\)](#) showed that the rate of impact-vaporization of Ca in Mercury's regolith by impacts of interplanetary dust and cometary dust, and its variation with true anomaly angle, are consistent with the observations ([Burger et al., 2012, 2014](#)). They did not discuss the physical state of the ejecta or pathways for energization of the calcium. In this paper we begin with the assumption that the initial vapor phase of calcium-bearing ejecta is CaO (e.g. [Berezhnoy and Klumov, 2008](#)). The equilibrium fraction of gas-phase Na-, K- and Ca-containing species released as a result of impact of a CI meteorite onto Mercury was calculated by [Berezhnoy and Klumov \(2008\)](#), assuming that the elemental composition of the mercurian regolith is a mixture of 90% plagioclase and 10% pyroxene by volume. At 3000 K, atomic Ca was found not to be a significant fraction of the gas-phase debris, rather Ca (OH)₂ dominates. At temperatures above 3750 K, CaO was found to dominate over atomic Ca and Ca(OH)₂. In addition to the equilibrium chemistry calculations of [Berezhnoy and Klumov](#), laboratory experiments have been conducted using laser ablation to simulate high-energy impacts. (CaO)_n clusters, where n can be 1 or more, were found ([Ziemann and Castleman, 1992](#)) and are shown to be possible precursor molecules for the hot Ca seen in Mercury's exosphere. In the remainder of this paper we assume that CaO is the initial form of the calcium ejecta, that it is ejected by impacts and that the initial fireball has a temperature >3750 K.

3. Processes producing hot calcium

3.1. Electron impact dissociation

CaO produced by impact vaporization at 4000 K has an energy of 0.3 eV, or a mean velocity of ~ 1.0 km/s. Having only one quarter of escape velocity it cannot directly escape, and most likely it sticks to the surface upon impact. Because CaO is highly reactive, the CaO will react with the surface minerals before the molecule is hit by another micrometeorite. Here we consider the possibility that CaO molecules produced by meteoritic impact are subsequently dissociated in the exosphere by electron impact.

The MESSENGER Energetic Particle Spectrometer (EPS) has sampled energetic electrons (10s of keV) at most Mercury longitudes and local times, and found that the largest burst events were either

at high northern latitudes or near local midnight ([Ho et al., 2012](#)). Lower-energy events were seen near the equator at all longitudes but with the highest concentrations in the dawn–dusk sectors ([Ho et al., 2015](#)). These lower energy events may be related to the quasi-trapped population in the equatorial region found in simulations by [Schriver et al. \(2011\)](#). For both northward and southward IMF simulations, [Schriver et al. \(2011\)](#) show that electron fluxes can be as large as 10^9 – 10^{10} cm^{−2} s^{−1} at some locations. On average, however, the observed electron flux is about 10^7 cm^{−2} ([Ho et al., 2015](#)).

For southward IMF, maximum precipitation fluxes in the [Schriver et al. \(2011\)](#) simulations tend to occur at the equator on the dawnside region, although there is also substantial precipitation in the northern hemisphere. Also for southward IMF, dayside reconnection occurs at lower latitudes over a broader region in longitude. When electrons pass through the reconnection region they tend to gain more energy with more spread in pitch and phase angle, which leads to a wider precipitation region in both latitude and longitude. The MESSENGER Fast Imaging Plasma Spectrometer (FIPS) detected MeV electrons during solar energetic events over the entire polar cap down to a latitude of 50° at midnight and again in the low latitude plasma sheet on the nightside of the planet ([Gershman et al., 2015](#)). They inferred from these measurements that the entirety of Mercury's polar caps are continuously bombarded by ~ 100 eV strahl solar wind electrons at fluxes of 10^7 – 10^9 cm^{−2} s^{−1}.

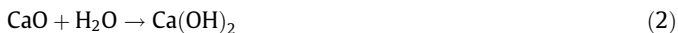
The electron impact dissociation cross sections of CaO were recently measured by [Miles \(2015\)](#) and are on the order of 0.4×10^{-16} cm² at 1 keV. This is similar to electron impact dissociation cross sections of other oxygen-bearing molecules by 100 eV electrons ([McConkey et al., 2008](#)). If CaO is produced by impact vaporization, a reasonable estimate of the column abundance of CaO, $N(\text{CaO})$, is about $2. \times 10^9$ cm^{−2} based on impact vaporization rates from [Cintala \(1992\)](#), using a calcium fraction of 0.035 in the regolith ([Weider et al., 2015](#)), assuming that all of the calcium is ejected as CaO ([Berezhnoy and Klumov, 2008](#)), and that its lifetime is the ballistic lifetime of the CaO molecule (760 s). Then the *e*-impact dissociation rate of CaO equals the production rate of Ca and is on the order of

$$\begin{aligned} \frac{d(\text{CaO})}{dt} &= N(\text{CaO})F(e)\sigma \\ \frac{d(\text{Ca})}{dt} &\leq 2 \times 10^9 \times 10^9 \times 0.4 \times 10^{-16} \end{aligned} \quad (1)$$

where $F(e)$ is the electron flux and σ is the *e*-impact dissociation cross section. If $F(e)$ is between 10^7 electrons cm^{−2} s^{−1} (background) and 10^9 (sporadic), using either the [Ho et al. \(2012\)](#) estimates for 100 eV to 1 keV electron flux or [Schriver's et al. \(2011\)](#) simulation results, the production rate of Ca by this process is ~ 80 atoms/cm²/s. The Ca photoionization rate at 1 AU is 6.96×10^{-5} s^{−1} during normal (quiet) solar conditions (W.F. Huebner and J. Mukherjee, Photo rate coefficient database, 2011, <http://phidrates.space.swri.edu>). Over the course of a Mercury year, the Ca photoionization lifetime at Mercury varies between 23 and 52 min due to Mercury's changing heliocentric distance in its eccentric orbit. If the lifetime of neutral Ca is the photoionization lifetime, 1345 s at perihelion to 3107 s at aphelion, the column abundance of Ca would be $<1 \times 10^5$ cm^{−2}. Thus using the most optimistic values, this result is 3 orders of magnitude too low compared with the observed Ca column abundance, 1.5×10^8 cm^{−2} (e.g. [Killen et al., 2005](#)). We do not expect that either the cross section or the electron flux is in error by orders of magnitude. Thus it is unlikely that electron impact dissociation is the cause of the hot calcium.

3.2. Spontaneous dissociation

Solid CaO does not vaporize to CaO but dissociates to Ca + O (Chase et al., 1998, JANAF Tables). The dissociation energy is 91 ± 5 kcal/mol, or 3.95 eV/molecule. Although it is likely that some of the CaO in an impact fireball will spontaneously dissociate, dissociation is always endothermic. Berezhnoy and Klumov (2008) and Ziemann and Castleman (1992) have stated that the CaO clusters are stable at these temperatures. However, the reaction



is exothermic and releases 64.8 kJ/mol, and has a time scale of 10^{-7} s at 3000 K (Berezhnoy and Klumov, 2008). This would raise the temperature in the fireball to 7800 K, well above the temperature at which CaO spontaneously dissociates. Ca(OH)_2 appears to be produced at temperatures in the fireball less than ~ 3500 K. The mixing ratio of atomic Ca and CaO both rapidly increase as the fireball temperature increases above 3000 K, while the mixing ratios of Ca(OH)_2 and H_2O decrease (Berezhnoy and Klumov, 2008). However, the energy in the fragments is less than 1 eV/atom, and is not sufficient to accelerate the atomic Ca to the altitudes where it is observed.

3.3. Dissociative ionization

High yields are found for impact ionization and dissociative impact ionization of dust particles and regolith for high velocity impacts such as those for comets and comet streams (e.g. Horning et al., 2000). Dissociative charge exchange has been observed in ion–molecule collisions. Dissociation following ionization is a likely pathway for spontaneous dissociation (Sidis, 1989). CaO clusters would be expected to readily evaporate after ionization, carrying away excess energy. Using a high-power laser to simulate a shock-induced vapor cloud, Kurosawa et al. (2010) reported shock-induced ionization on diopside ($\text{CaMgSi}_2\text{O}_6$). Of interest here is not only the ionization but the temperature of the shock-induced vapor cloud, measured to be $>20,000$ K, consistent with the temperature of the Ca exosphere estimated from the measured line widths of the Ca exosphere from ground-based spectroscopy (Killen et al., 2005) and with MASCS results (Burger et al., 2014). Note that the mean impact velocity for micrometeoritic impact onto Mercury was estimated to be 20.5 km/s (Cintala, 1992), and shock-induced ionization has been observed as a result of impacts at velocities >10 km/s. Although the peak impact velocity at Mercury was estimated by Cintala (1992) to be about 20 km/s, Marchi et al. (2005) calculate that the meteoritic flux at Mercury should have a peak at 30 km/s and an additional peak at about 42 km/s. If so, then significant shock-induced ionization would occur. Although Horning et al. (2000), using a hydrocode to simulate impacts, do not show significant ionization of Si and O until impact velocities are in excess of 60 km/s (the ionized fraction of Si was calculated as 14% for an impact velocity of 60 km/s), laboratory experiments (Knabe and Krueger, 1982; Krueger, 1996) show that there is charge production from the impacting particle as well as from the target already at a few km/s. Using a conservative estimate based on the Cintala (1992) velocity distribution, 17% of the incoming meteoritic dust is above 40 km/s. Then we would conservatively estimate that $<1\%$ of the vapor is ionized and dissociates. Although it is expected that 99% of the plasma recombines in the first nanosecond, producing an optical flash, the collisionless plasma is expected to expand at 15 km/s (Starks et al., 2006). Given a rate of vaporization of $\sim 3 \times 10^6$ Ca-bearing molecules or atoms $\text{cm}^{-2} \text{s}^{-1}$ (Killen and Hahn, 2015), 0.85% of this is $2.5 \times 10^4 \text{ cm}^{-2} \text{s}^{-1}$. If the lifetime of Ca in the exosphere is the photoionization lifetime (1345 s at perihelion), then the column would be

$<4 \times 10^7 \text{ cm}^{-2}$ which is less than one third that which is observed. Ions are rapidly accelerated in the electric fields at Mercury. Plasma expansion speeds for impacts on uncharged tungsten peak near 20 km/s and have a distribution between 10 and 30 km/s (Lee et al., 2012). Given uncertainties in the velocity distributions, the ionized fraction and the ionization lifetime, dissociative ionization is a likely process for producing at least some of the hot Ca at Mercury.

3.4. Photodissociation

The photodissociation rate has not been measured for CaO. (Another potential precursor molecule is CaS, given the low oxygen abundance and high sulfur content of the regolith (e.g. Weider et al., 2015).) Calculation of photodissociation rates requires knowledge of the molecular states, their oscillator strengths, the dissociation efficiency of the upper level and the fractional population of the lower level. Such calculations have been done for molecules of astrophysical interest but not for CaO. However, the photodissociation rates of diatomic molecules in Huebner and Mukherjee (2015) are between 1.0×10^{-4} and $1.0 \times 10^{-8} \text{ s}^{-1}$ at Earth orbit, and would be $1/R^2$ faster at a heliocentric distance, R . Therefore, we can place limits on the photodissociation rate that can be obtained for Ca-bearing diatomic molecules based on this range of probable rates.

If we assume that the total impact vaporization rate for all atomic species is $\sim 7 \times 10^7 \text{ atoms cm}^{-2} \text{s}^{-1}$ at perihelion (Cintala, 1992) and the Ca fraction is 0.035, then given a ballistic lifetime of ~ 760 s estimated from a temperature of 3000 K (e.g. Hunten et al., 1988) we obtain a column of CaO of $\sim 2. \times 10^9$. Let the photodissociation rate be between 10^{-4} and $10^{-8}/R^2$ /molecule/s, where R is the heliocentric radial distance. At Mercury perihelion, the photodissociation rate is then between 10^{-3} and 10^{-7} s^{-1} . The most optimistic production rate for Ca along with a photoionization lifetime, $\tau(\text{Ca})$, of 1345 s at perihelion gives a Ca column of

$$\begin{aligned} \frac{d\text{Ca}}{dt} \tau(\text{Ca}) &= 2. \times 10^9 \times 1. \times 10^{-3} \times 1345 \\ [\text{Ca}] &= 2.7 \times 10^9 \text{ cm}^{-2} \end{aligned} \quad (3)$$

The observed column abundance of Ca is $1.5 \times 10^8 \text{ cm}^{-2}$ (Killen et al., 2005), which would require a photodissociation rate of $7.5 \times 10^{-5} \text{ s}^{-1}$ at perihelion or $7.0 \times 10^{-6} \text{ s}^{-1}$ at Earth. This is consistent with photodissociation rates of CH and CO from Huebner and Mukherjee (2015). The binding energy of CaO (4.5 eV) (Markandey and Chaturvedi, 1987) falls between those of CH (3.45 eV) and CO (11.1 eV). The excess energy of photodissociation of CO is about 2 eV, and that of CH is about 0.2 eV. To conserve momentum, the velocity of Ca is 40% that of O. An optimistic estimate of the excess energy for CaO is about 2 eV. If Ca carries off 40% of 2 eV that would be 0.8 eV. If Ca already has a velocity of about 1 km/s then the average Ca velocity would be ~ 2 km/s, which is about half escape velocity.

Why should hot Ca preferentially appear on the dawnside hemisphere given that the solar flux peaks at the subsolar point? We propose that the impact vaporization, the primary source of Ca-bearing molecules in the exosphere, peaks near the equator on the dawnside hemisphere, in the ram direction, as it does at Earth (e.g. Janches et al., 2006) and at the Moon (Horanyi et al., 2015). In that case, we would preferentially see hot Ca on the dawnside because that is where the molecules are preferentially ejected into the exosphere by impact vaporization and subsequently dissociated, and where they are excited into the first excited state by the incoming solar flux.

3.5. Sputtering

An additional way to obtain hot Ca is sputtering. Kinetic energy distributions of sputtered Ca, Ca₂, and Ca₃ are quite similar, with a maximum near 1 eV and a slope of -2 for Ca and -4 for Ca₂ at high energies. It is significant that the flux of Ca ejected at 10 eV is only about a factor of 3 less than the flux ejected at 1 eV (Hansen et al., 1998). If sputtering were the primary source process for Ca, its energy would not necessarily be a problem. However, energetic charged particles are mostly deposited on the surface through the magnetic cusps and on the nightside, not at the equator and not just in the dawn hemisphere (Raines et al., 2013).

4. Discussion

Due to the small cross sections for electron-impact dissociation we conclude that it is not a possible pathway to create hot Ca at Mercury. Spontaneous dissociation of hot CaO is possible, especially if the CaO is ionized by charge exchange (Sidis, 1989) but the energy is not expected to be as large as that observed. Shock-induced dissociative ionization followed by neutralization is a possible pathway given that the mean impact velocity of micrometeoritic dust at Mercury is 20.5 km/s or more. This is observed to produce hot vapor at about 20,000 K, which is consistent with the temperature observed by Killen et al. (2005). The observed mean velocity from impact shocks is about 15 km/s, consistent with a temperature of 54,000 K which is well within uncertainties of that estimated by Burger et al. (2014). Our estimate is that at least 30% of the observed hot Ca could be produced by this method. However, given uncertainties in the impact velocity distribution, shock induced ionization rate, and dissociation probability, this is a viable process.

The final method considered, photo-dissociation of CaO, can be ruled out because observations show that part of the source of hot Ca is produced in the shadow behind the terminator where photons cannot have access (Burger et al., 2014). In addition this method probably produces Ca at half escape velocity.

If sputtering were the primary source process for Ca, its energy would not necessarily be a problem. However, energetic charged particles are mostly deposited on the surface through the magnetic cusps and on the nightside, not at the equator and not just in the dawn hemisphere (Gershman et al., 2015). The Na⁺-group ions show an enhancement at high latitudes, centered at local time ~ 10.5 h, which corresponds, at least in part, to the northern magnetospheric cusp (Raines et al., 2013). Therefore we reject sputtering as a primary source of hot Ca based on the observed peak production rate for Ca at the dawn equator, not at the poles or cusps. Nevertheless we acknowledge that a sputter distribution is not inconsistent with the observed energy.

The dissociative double photoionization processes induced by VUV and EUV photons leading to the production of fragment ions with a high kinetic energy content has been proposed as an important pathway for ion species escape from the atmosphere of some planets of the Solar System, like Venus, Mars and Titan (Falcinelli et al., 2014). In the case of Ca at Mercury, however, there is the additional problem of neutralization of the Ca⁺ fragment. It has been estimated that neutralization could occur within nanoseconds of the initial impact.

5. Conclusions

The most likely origin of extremely hot Ca seen in Mercury's exosphere is dissociative ionization of a precursor CaO molecule or clusters, or possibly some other diatomic molecule such as CaS, produced by impact vaporization. Shock-induced vaporization due to cometary streams may be capable of producing hot vapor at

20,000 K or higher and would result in substantial ionization of fragments. It has been shown that CaO clusters and even dimers are produced by vaporization of diopside, and that the dawnside origin of the Ca is the result of preferential impact vaporization in the ram direction as Mercury moves through the interplanetary medium. MESSENGER UVVS observations (Burger et al., 2014), and simulations of CaO breakup (Killen, 2015) show that production of hot Ca is occurring behind the terminator in the shadow, ruling out photodissociation as a significant process. Electron impact dissociation is ruled out due to insufficient electron flux in Mercury's dawn equatorial region where the Ca source appears.

In addition to Ca, there has been some indication that Mg in Mercury's exosphere is perhaps as hot as 20,000 K and may be concentrated in the dawn hemisphere (Sarantos et al., 2011). Some of the arguments put forth for Ca may also apply to Mg (Ziemann and Castleman, 1991).

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